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CONTAINING ACTIVE OXYGEN

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# THE PRODUCTION OF GASEOUS OXYGEN FROM SALTS CONTAINING ACTIVE OXYGEN

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**ABSTRACT:** Describes small scale production of high-purity oxygen for special applications, starting from chlorates or alkali peroxides.

In the field of commercial oxygen production, physical processes have completely displaced chemical ones. Moreover, in many chemical plants, oxygen is available at nearly no cost and as a result it has become difficult to find profitable applications for it. Such an application used to be, for example, the enrichment of combustion air with oxygen. For this reason, there is no incentive to use the markedly more expensive chemical processes. A rough estimate of the cost of oxygen made by chemical and physical processes shows that 1 m<sup>3</sup> of O<sub>2</sub> made from alkali chlorates and perchlorates costs about 1.30 - 1.50 RM (Reichsmark), and 5 - 7 RM when made from hydrogen peroxides alkali peroxides, alkaline earth peroxides and perborates; by contrast, compressed oxygen costs 0.50 - 0.60 RM / m<sup>3</sup>. /553\*

Nevertheless, chemical methods for the production of oxygen have recently again received increased attention, although not as competitors of the low temperature processes but as oxygen sources in a few special fields where the use of compressed oxygen has certain disadvantages. The high-pressure steel cylinder represents a large dead weight for which shipping costs must be paid twice, i.e., on the way to and from the consumer. In particular, when cylinders must be shipped long-distance overland or overseas, shipping costs exceed the cost of oxygen. In the case of large 40 - 1 cylinders weighing 76 - 80 kg and containing about 6.5 m<sup>3</sup> of oxygen, the dead weight exceeds the weight of oxygen by a factor of about 10, this factor being higher for smaller cylinders and twice as high for the empty return cylinders. This problem has not been resolved by the recent introduction by "Rheinmetall" of light-metal cylinders (Lautal) which represent a reduction in weight of about 40 % because the cylinders are very expensive and at the present time are commercially available only in sizes up to 2 liters. Furthermore, the acquisition, ammortization and maintainance (official pressure tests) of a large inventory of pressure cylinders represent a sizable expense which the oxygen manufactures must pass on to the consumer in the form of not insignificant cylinder rental charges. Large oxygen consumers endeavor to reduce these expenses (shipping of dead weight, cylinder rental, maintainance of their own cylinders) by transporting the oxygen in the liquid state. The effect of this, however, is minor because the above-cited expenses tend to affect the small consumer relatively much more than the large consumer.

Among these small consumers are various craftsmen who require small quantities of oxygen for occasional welding and metal cutting operations and places using

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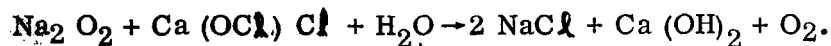
\* Numbers in the margin indicate pagination in the foreign text.

O<sub>2</sub> for breathing protection and medical purposes, i.e., mainly physicians, hospitals (O<sub>2</sub> treatment of the respiratory tract and lungs, anesthesia, etc.) and mines, fire departments, the military and the Red Cross (for protection against toxic gases and resuscitation). In these applications, oxygen use-methods based on high-pressure devices represent a considerable expense which, of course, increases with increasing distance from oxygen manufacturing centers; even in industrial cities with oxygen plants, there are numerous cases where the cost of the oxygen consumed is entirely out of proportion to the expense imposed by high-pressure apparatus. This is true particularly for the gas protection and medical fields where the cost of oxygen is secondary to the requirements of immediate preparedness, ready availability and light weight, simple and inexpensive apparatus.

These requirements can be largely met by use of chemical processes. These processes, however, do not include those previously used for the large scale production of oxygen wherein the chemicals employed, after giving off, in a concentrated form, the oxygen absorbed from the air ( $\text{BaO} \rightarrow \text{BaO}_2 \rightarrow \text{BaO}$ ), had to be regenerated for economic reasons. As indicated above, current problems require above all smooth, simple and reliable formation of high-purity oxygen while the possibility of regeneration the chemicals used is of no importance.

The selection of the chemical process for solving this problem will be different depending on whether the chemicals are required only for oxygen generation, for example, in autogenous metal treatment and for medical purposes, or whether the process must also satisfy other needs, such as, for instance, the removal of CO<sub>2</sub> from the exhaled air in gas protection devices. Particularly suitable for the latter purpose are alkaline compounds, for example, alkali peroxides, whereas chlorates and perchlorates, because of their low price and stability in air, should be better suited for the former application. However, technical difficulties have prevented their use. Their decomposition is not as easy and smooth as that of compounds containing active oxygen in the form of a peroxide bond, i.e., hydrogen peroxide, alkali peroxide, perborates, etc. In the presence of suitable catalysts, these compounds readily generate oxygen of high-purity. Because of the danger of handling concentrated hydrogen peroxide solutions required for the generation of gaseous oxygen, the use of hydrogen peroxide is restricted to oxygen baths and inhalation therapy of the respiratory tract and lungs [1]. Sodium peroxide, particularly when mixed with chlorinated lime and compressed into cubes, a form known under the name of "Oxylith" (Jaubert [2]) has achieved considerable importance in autogenous metal treatment and for laboratory purposes. These cubes react with water generating twice the amount of oxygen obtainable from pure (and expensive) Na<sub>2</sub>O<sub>2</sub>. The reaction occurs according to the following scheme:

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A shortcoming of this system is that it produces highly corrosive hydroxides.

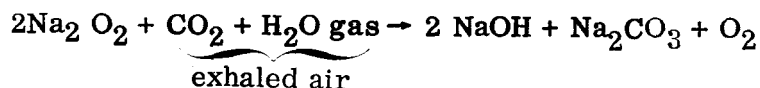
This defect was recently eliminated by the introduction of "Oxygal" which allegedly also contains Na<sub>2</sub>O<sub>2</sub> as the active oxygen salt [3]. This product, however, does not generate oxygen by reaction with water but by a thermal process with the aid of a special ignition powder and a match. One kilogram of Oxygal generates about 240 l of O<sub>2</sub> which is stored in a pressure container, whence it is withdrawn through a pressure reducing valve.

Chlorates and perchlorates also generate oxygen thermally and in the presence of catalysts ( $MnO_2$ ,  $Co_2O_3$  etc.) capable of reducing the recombination temperature by about  $200^\circ C$ . Sudden reactions are prevented by addition of inert diluents (diatomaceous earth, pumice). Decomposition of the briquetted mixtures (Jaubert, Zeiss [4] is initiated by ignition. The briquettes are then enclosed in steel cylinders where oxygen is generated to a pressure of about 30 atm. Oxygen produced in this manner is, however, not sufficiently pure; it always contains a small amount of chlorine which makes it unsuitable for breathing purposes and strongly corrodes the metallic parts of the apparatus; furthermore, it contains chloride dust particles which sublime as a result of the vigorous reaction, are entrained by the gas and tend to plug the gas lines.

In the recently introduced "Naszogen" process [5], these defects of the use of chlorates are avoided by addition of exothermic compounds which serve the purpose of removing a part of the rather considerable heat of reaction, thereby controlling the reaction within desired limits. As a result, pure oxygen is obtained in a desired amount per unit time and at an approximately constant rate. In many cases, storage under pressure can, therefore, be avoided. This amounts to a total replacement of high pressure equipment.

It should also be noted that the combustion gas required for autogenous metal treatment can be obtained by known methods from calcium carbide or by vaporization of liquid fuels, e.g. benzene (Fernholz process), namely without the use of pressure cylinders.

The requirements which the processes for oxygen generation in gas protection devices must satisfy are different. Processes based on oxygen formation by action of a liquid on a solid, for example, by dropwise addition of water to mixtures containing alkali peroxides, are not used for this purpose. This is because the constant change in position of portable gas protection devices would make such a process unreliable. Furthermore, as already mentioned, absorption of carbon dioxide from the exhaled air constitutes a second chemical function besides oxygen generation. Alkali peroxides seem to be predestined for this use. They react according to the scheme



and thus, in one reaction, satisfy the requirement for oxygen regeneration and carbon dioxide absorption, i.e. they act as a "chemical equivalent" of the lungs. The technical realization of this idea of a chemical oxygen breathing device is based on passage of the oxygen-depleted, carbon dioxide-rich exhaled air through cartridges containing alkali peroxides in granular form. In these cartridges, the respiratory air is "regenerated" i.e., it is freed of carbon dioxide and enriched with  $O_2$ , so that it can be reused. Potassium sodium peroxide which before and during World War I was used under the trade name "Pneumatogen" had the disadvantage that the granules fused together because of the high reaction temperature ( $200^\circ C$ ) thereby increasing the breathing resistance to unacceptable values (above 75 mm  $H_2O$ ). During and after the war, potassium sodium peroxide in the "Proxylon" apparatus was replaced with sodium peroxide containing 6 % of water. Because of its limited storage stability, this hydrated product was also unsatisfactory [6]. Attempts have been made recently to increase the stability of these hydrated

peroxides by a short heat treatment. Devices wherein  $\text{CO}_2$  generation is initiated with the aid of  $\text{CO}_2$  from a small pressure cylinder are also not used in emergencies.

Because of the great difficulties encountered in attempts to combine in one step the generation of oxygen and the absorption of carbon dioxide, these two reactions have been separated. This, according to the new, above-described "Naszogen" process, oxygen is produced from chlorates in a manner independent from the breathing rate and in amounts exceeding maximum  $\text{O}_2$  requirements (vigorous exertion), while carbon dioxide is removed by reaction with caustic soda in separate cartridges. These devices also must prove themselves in practice.

At the outset, a distinction was made between large and small consumers. This, however, does not mean that the economic importance of the small consumers is slight. On the contrary, in the field of autogeneous metal treatment, the craftsmen consuming small quantities of oxygen all together certainly account for an appreciable proportion of the oxygen consumed. In the field of gas protection, however, chemical oxygen breathing devices certainly play a leading role. Such equipment constitutes the personal gas protection device of a miner or a fire fighter. The goal set at various international rescue meetings to provide every miner working underground with his own protection device could thus far not be reached mainly because of financial and also because of technical reasons. The solution of this problem by means of chemical oxygen devices is only a question of time.

#### REFERENCES

1. German Patent nos. 429,040 and 430,550.
2. German Patent nos. 140,574 and 143,542
3. Chemiker-Zeitung, p. 40, 1933.
4. German Patent nos. 223,246 and 259,575
5. Jour. Appl. Chem., Vol. 43, p. 732, 1930.
6. Ibid., Vol 46, p. 45, 1933.

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